SELF-ASSEMBLY TEMPLATES BY SELECTIVE PLASMA SURFACE MODIFICATION OF MICROPATTERNED PHOTORESIST

Jeonggi Seo, Elif Ertekin, Michael S. Pio, and Luke P. Lee

Berkeley Sensor & Actuator Center and Department of Bioengineering
University of California at Berkeley, CA94720, USA
Phone: (510) 643-3389, Fax: (510) 643-6637, E-mail: seojohn@uclink.berkeley.edu

ABSTRACT

Self-assembly templates, consisting of micro-patterned hydrophobic and hydrophilic regions, are fabricated using a plasma surface modification technique. With exposure to O_2 plasma, photoresist, silicon, and glass can be modified to hydrophilic surfaces. When followed by SF_6 or CF_4 plasma, the surface of photoresist can be modified to hydrophobic while silicon and glass surfaces are not affected. The difference in surface energy between the hydrophilic and hydrophobic regions is large, as indicated by the differential contact angle of 120° between the two regions for wetting with water. Photonic crystals are made from colloidal solutions and protein patterning is demonstrated using self-assembly templates made by selective plasma surface modification. The maximized surface energy difference between substrate and template patterning allows an ideal self-assembly of photonic crystals and selective attachment of proteins.

INTRODUCTION

Recently, several authors have demonstrated the fabrication of microlenses [1-2] and assembly of micromirrors [3] using hydrophobic effects. Other authors have characterized cell adhesion on hydrophilic and hydrophobic surfaces [4], but they used complicated methods to make the surfaces using fluoropolymers (i.e. Teflon® or Cytop®). These methods require deposition of fluoropolymers, micropatterning, etching fluoropolymers, removing photoresist without damaging patterned areas, and annealing fluoropolymers to render a surface hydrophobic. Protein patterning using photoresist layers was also demonstrated by Nicolau *et al.* [5]. They used exposed and unexposed photoresist to obtain different surface energies. However, their photoinduced surface hydrophobic manipulation was not selective enough for effective protein patterning; the difference in hydrophobicity of the surfaces was small, as indicated by the differential contact angle of 15° for wetting with water. Photonic crystals made from colloidal solutions were fabricated [6] by Ye *et al.* with evaporation methods. However, with their methods, there is no way to pattern the photonic crystals while maintaining high crystal quality. Clearly, the development of an effective technique to selectively pattern hydrophilic and hydrophobic surfaces is useful for a broad range of applications.

This report addresses the need for a simple technique to pattern hydrophobic and hydrophilic surfaces. Upon exposure to various plasmas, the surface properties of photoresist layers, silicon, and glass can be modified, enabling the fabrication of self-assembly templates. A self-assembled photonic crystal is formed from colloidal particles and protein patterning is demonstrated using these self-assembly templates. Selective plasma surface modification of photoresist layers will enable low-cost, simple fabrication steps, with IC-compatible processes for self-assembly.

SELF ASSEMBLY TEMPLATES

Plasma surface modification is used to fabricate self-assembly templates consisting of patterned hydrophilic and hydrophobic regions, as illustrated schematically in Fig. 1. With selective modification of pattered photoresist, the self-assembly templates can be created by exposure to O_2 and SF_6 plasmas. Compared with other methods, this is simple and low-cost, because our method does not require coating and etching hydrophobic materials.

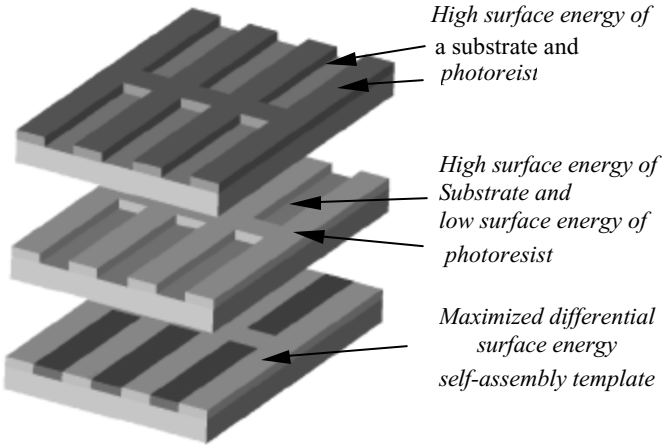

Figure 1. Self-assembly template using selective surface modification

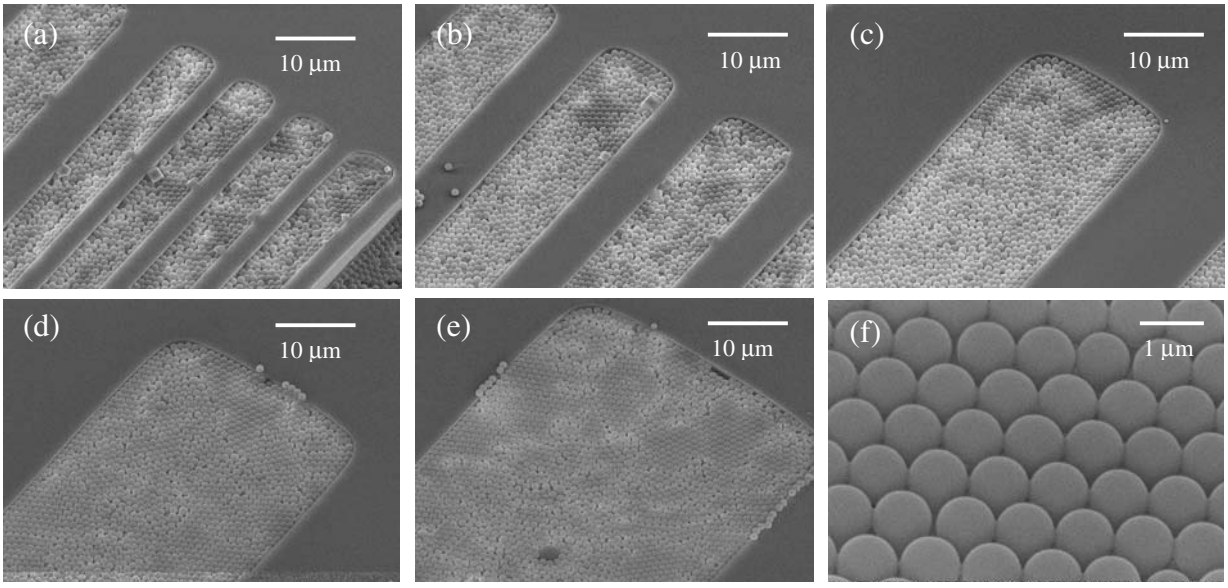

Figure 2. 3D photonic crystal generated in self-assembly templates with selective plasma surface modification :(a) 7μm, (b) 12μm , (c) 22um, (d) 32μm , (e) 42μm width of self-assembly template, and (f) magnified image of crystal.

Self-assembly of microlens arrays on glass substrate with patterned photoresist modified by plasma was demonstrated earlier [7]. Self-assembly templates were prepared with selective plasma modification of micro-patterned photoresist. UV-curable polymers were coated on the substrate. Because of different surface energies of modified surface, microlenses formed only on the patterned areas.

Here, three-dimensional (3D) photonic crystals fabricated on the self-assembly templates with 0.923 μm diameter beads are demonstrated. The self-assembly templates were prepared with the same method as with the microlens arrays. The microbead solution was spin-coated at 5000 rpm for 5 seconds on the templates, and the solution was allowed to dry by evaporation. The beads accumulated only on the hydrophilic patterned silicon areas. Using this method, photonic crystals were made, as shown in Fig. 2.

Additionally, selective attachment of proteins using the templates is also demonstrated here. Collagen solution (BD Science, type 1 rat tail, 1.05mg/ml in acetic acid) was spin-coated at 5000 rpm for 5 seconds. The proteins accumulated only on the patterned hydrophilic areas as shown in Fig. 3.

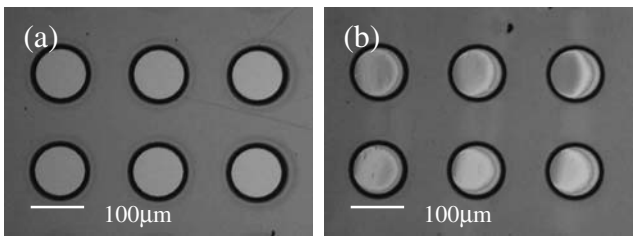

Figure 3. Selective attachment of Collagen solution (a) before and (b) after.

FABRICATION OF SELF ASSEMBLY TEMPLATE

Plasma surface modification of photoresist

To prepare the self-assembly templates on micro-patterned photoresist layers, the silicon or glass surface must be made hydrophilic while the photoresist should be hydrophobic: this is the purpose of plasma surface modification. Photoresist layers hard baked at 120°C for 2 hours were exposed to SF_6 or CF_4 plasma. During the modification, the chamber was maintained at 180 mTorr and the flow rates of SF_6 and He were 13 sccm and 21 sccm, respectively. The plasma power was 100 W. For consistency, all plasma modifications with SF_6 were done with the same condition except for time of modification.

To evaluate the effectiveness, the contact angle of water on photoresist layers before and after modification was measured. The surface tension σ_s of an interface is determined by the measured contact angle and known surface tension σ_l of test fluids. This determination technique is based on Young's equation. At the three-phase point, three interficial tensions should be in equilibrium [8].

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos\theta \qquad (1)$$

If the contact angles of the same test liquid on each surface are measured, the surface free energy of each surface can be compared.

The contact angle of water and polymer on photoresist layer (Shipley STR 1075) was measured before and after the modification. The contact angle of polymer (Norland 121) after hardbaking was 37.9°. But after modification the contact angle increased to 60°. The contact angles of

water had the same tendency as that of polymer. The contact angle of water on photoresist increased from 74.9 ° to 110°, which is the same as the contact angle of a water droplet on Teflon® [9]. Thus, we could modify a hydrophilic surface to a hydrophobic surface.

To test the stability of plasma modification, 9 μm thick photoresist layers were spin-coated on silicon and glass substrates, patterned, and backed at 120° C. After 1 minute O_2 and 1 minute SF_6 plasma surface modification, the contact angles were measured for 30 days as shown in Fig. 4. The substrates were kept in atmospheric conditions with no control of humidity and temperature. After 30 days, there was no significant degradation of hydrophobicity on the photoresist layer.

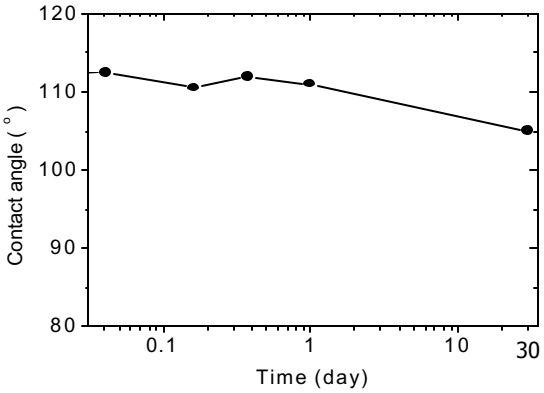

Figure 4. Stability of plasma surface modification on each layer with time. (O_2 100W 1min and SF_6 100W 1min)

Selective modification of patterned photoresist

Shipley, STR 1075 photoresist was spin-coated on silicon and glass substrates, patterned, and baked at 120°C. The contact angles on bare substrates and photoresist layers were measured (Table 1). After one minute 100W O_2 plasma modification, the contact angle on each substrate decreased to between 0° and 10°. With consecutive 100W CF_4 or SF_6 plasma modification, the contact angle dramatically increased to 114.1° only on the photoresist layer. However the contact angle on the silicon and glass wafers did not increase. With this method, surfaces of patterned photoresist were selectively modified as shown in Fig. 5. O_2 plasma modification was used to make the surface of silicon or glass substrate more hydrophilic. CF_4 or SF_6 plasma was used to make photoresist more hydrophobic. Without O_2 plasma modification, CF_4 or SF_6 plasma modification made 100° differences in the contact angle of water between photoresist and silicon. However, O_2 plasma modification followed by CF_4 or SF_6 plasma modification, the difference in contact angle between the modified photoresist layer and silicon substrate increased to 120° as shown in Fig. 6.

Factors for modification

Wenzel reported the relationship between surface roughness and contact angle in 1936 [10]. He explained

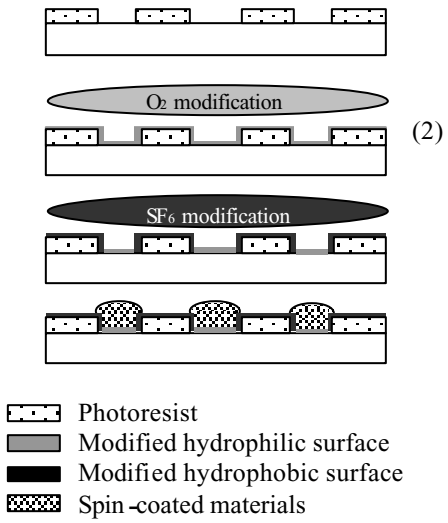

Figure 5. Self-assembly templates by selective plasma surface modification: (a) Patterned and hardbaked photoresist, (b) O_2 modification to make hydrophilic surfaces, (c) SF_6 modification to make hytdrophobic surfaces, (d) Attached materials only on hydrophilic areas because of differential surface energies.

Table 1. Contact angle on substrates

	Bare*	O2 modification	After O2 and SF6 modification
Contact angle of water			
Si	26.1	–	–
Oxide	28.1	–	–
STR1075	74.9	8.1	114.1
Contact angle of water			
Si	14.9	7.1	6.9
Oxide	13.4	7.5	7.2
STR1075	37.9	6.3	62.0

*Bare means bare silicon, bare oxide, and hardbaked photoresist.

- The surfaces were totally wetted.

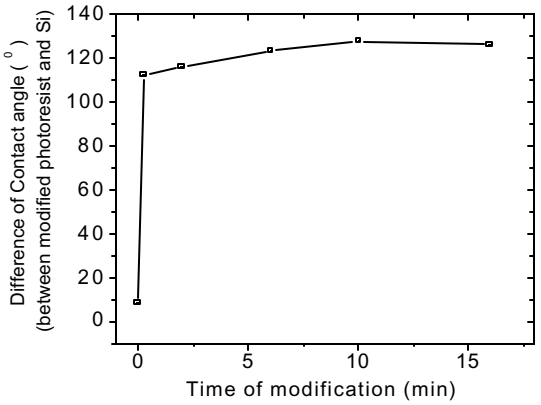

Figure 6. Difference between the contact angles on the modified photoresist layer and silicon substrate.

that the contact angle θ_r on a rough surface is related with the contact angle θ_s of a smooth surface and r, the ratio of the actual to projected area, by the expression

$$\cos\theta_r = r\cos\theta_s$$

Thus, on a rough surface, the contact angle θ_r is decreased by roughness when θ_s is less than 90°. If θ_s is greater than 90°, then θ_r should increases. Surface roughness of photoresist was measured with Atomic Force Microscopy (AFM) as shown in Fig. 7. We expected that plasma exposure would increase the roughness and result in a decrease in contact angle since the contact angle before modification was 74.9°. After hardbaking, root mean square (RMS) roughness was 0.28 nm. After consecutive 1, 5, 10, and 15 minutes SF_6 plasma surface modification, RMS roughnesses were 1.36 nm, 13.93 nm, 29.26 nm, and 33.01 nm, respectively, as shown in Fig. 8. As expected, the roughness increased with the time of modification. However, the contact angles increased as well: 115.7°, 123.4°, 127.4°, and 125.9°, respectively. This behavior is contrary to Wenzel's model. However, if only the behavior after the large initial increase in contact angle is considered, the Wenzel formulation appears to be a reasonable model. Thus, while the large initial shift in contact angle was most likely induced by chemical changes at the surface, the variation in the contact angle for larger modification times appeared to follow the Wenzel formulation.

The dependence of surface properties on hardbake temperature was also explored. We could not find large dependence because the difference of the contact angle before and after modification among the different hardbake temperatures was less than 10°.

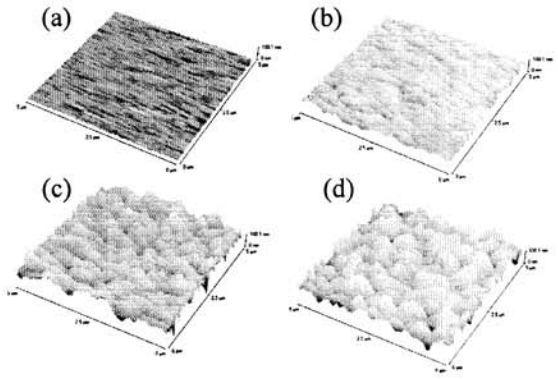

Figure 7. 3D image of surface roughness after 1 min SF_6 modification(a) and 1 min SF_6 modification(b).

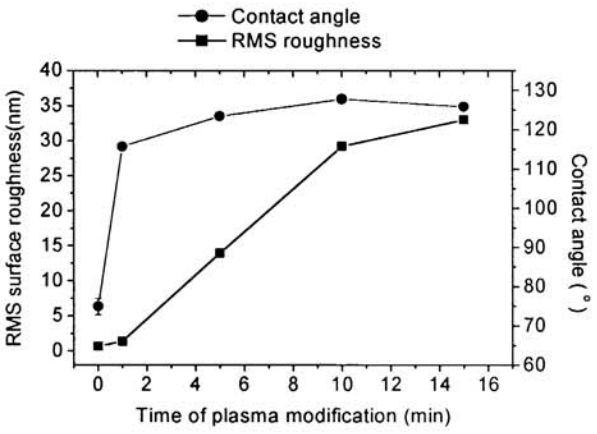

Figure 8. The relationship between RMS surface roughness and contact angle after SF_6 plasma modification

CONCLUSION

The plasma surface modification reported here has the potential to make self-assembly templates because of low-cost and simple fabrication steps. Selective plasma surface modification with photoresist layers is a new method to change surface properties selectively, allowing the fabrication of self-assembly templates. With selective plasma surface modification, self-assembly of microlenses, protein, and photonic crystal has been demonstrated. In the future, x-ray photoemission spectroscopy (XPS) measurements of modified surface will be otained to explain the large increase of the contact angle of water at the onset of modification.

ACKNOWLEDGMENTS

This work is funded by DARPA BIOFLIP program. The experiments and measurements were done in the Microfabrication Laboratory of University of California at Berkeley.

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